

STAGED COMBUSTION OF CHLORINE- AND NITROGEN-CONTAINING HYDROCARBONS FOR THE MINIMIZATION OF NO_x AND PIC'S

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This paper describes our current research in the area of staged combustion, wherein the overall fuel-lean system is divided into a fuel-rich (oxidant lean) first stage followed by a fuel-lean (oxidant rich) second stage. The first stage of our turbulent flow combustor is a jet-stirred, backmixed zone which can be modeled as a perfectly stirred reactor (PSR) under most conditions. The effluent from this zone enters a linear flow zone which can be modeled as a plug flow reactor (PFR). Industrial turbulent combustors, incinerators, and afterburners which employ a central fuel nozzle and swirled concentric air for flame stabilization can often be modeled with this sequence (Beer and Chigier, 1983).

This work utilizes an atmospheric pressure toroidal jet-stirred / linear flow two stage sequential combustor shown in Figure 1. The primary zone (torus) was first described by Nenniger et al., 1984. Premixed fuel gas and air are introduced at sub-sonic velocities into the torus around its outer circumference. The off-radial jets entrain the swirling bulk gas, causing a highly turbulent, backmixed condition. Residence times are typically 5-10 milliseconds in this 250 milliliter primary zone. The hot, reactive gases exit the torus, passing over a flow straightener into the secondary (linear) stage. Additional gases, typically air/O₂/steam in this work, are injected at this point. Second stage residence times are on the order of 20 milliseconds in this 30 centimeter long secondary zone. Stable species gas samples are withdrawn through two water-cooled probes. At present, all fuels are input to the reactor as gases. The primary fuel is C₂H₄. Fuel-bound chlorine and nitrogen sources simulating hazardous wastes are CH₃Cl and CH₃NH₂, respectively. A schematic of the entire facility is presented in Figure 2.

When CH₃Cl is burned, the sample gas is scrubbed of HCl in a gas-water countercurrent flow packed tower. The column is sufficiently oversized that effectively 100% HCl recovery from the inlet sample gas stream is achieved. The liquid effluent contacts chloride ion selective and reference electrodes used for HCl quantification.

The sample gas stream passes successively through a chilled bath for water vapor condensation, a droplet knockout, and a metal bellows pump, which provides the suction for sample withdrawal and the pressure head for sample passage to the various analyzers. The metered pump outlet sample gas is then split, with a portion flowing to O₂, CO, and CO₂ continuous emission analyzers and a gas chromatograph. The gas chromatograph is equipped columns for separation of light hydrocarbons and chlorocarbons, CO, and CO₂. The columns elute onto thermal conductivity and flame ionization detectors. The remainder of the sample gas passes through a gas drier, then flows to Total Hydrocarbon and NO_x analyzers.

There are three segments to the modeling of this combustor: elementary reaction mechanism, reactor simulation, and rate-of-production analyses. The first and second represent a major simplification of the turbulent fluid mechanics in favor of an emphasis on detailed chemistry. A favorable comparison of the experimental data and model predictions justifies the use of the third segment, which identifies the important chemical pathways.

For the experimental cases considered in this work, the reaction mechanism for the combustion of C₁/C₂ hydrocarbons and CH₃Cl is taken from Ho et al., 1992. The mechanism for CH₃NH₂ combustion and NO_x chemistry is taken from Miller and Bowman (1989), Sun et al. (1987), and Beer et al. (1981). Generated from the mechanism is ω_k , the net molar rate of production by reaction of species k, which is used in the reactor simulation equations.

The jet-stirred zone can be modeled under most conditions as a PSR, with the following governing species balance equations:

$$M(Y_k - Y_{k0}) = \omega_k W_k V \quad (1)$$

where M = mass flow rate, Y_k = mass fraction of species k (total of K species), W_k = molecular weight of k, and ω_k = net molar rate of production by reaction of k, V = reactor volume, and subscript 0 represents the feed condition. The linear flow zone can be modeled as a PFR, with the following governing species balance equations:

$$\frac{dY_k}{dt} = \frac{\omega_k W_k}{\rho} \quad (2)$$

where t = reaction (residence) time and ρ = mass density.

The mechanism is incorporated into a PSR+PFR reactor simulation program (driver code) which accesses the *CHEMKIN* package (Kee and Miller, 1986). The input to this driver includes composition, temperature, and mass rate of the PSR feed and post-PSR injection, reactor pressure, PSR volume and measured temperature, and PFR residence time and measured temperatures. Our driver program includes options to request net rate-of-production information for selected species to construct the chemical pathways involving reactants, intermediates, and products.

A series of runs were made to examine the effects of full staging on NO levels. A fuel-lean (equivalence ratio¹ $\phi = 0.86$) baseline was established. The feed to the primary stage was sequentially increased ($\phi = 0.86$ to 1.43) while the temperature was kept constant at 1760 K. The molar ratio of CH₃NH₂ to C₂H₄ in the feed was maintained at 0.058. For each fuel-rich PSR feed, air was injected into the secondary stage so as to achieve an overall combustor ϕ of 0.86. All concentrations reported for the PFR have been corrected upward for the dilution effect of the injected air.

¹ $\phi = [\text{fuel/air}]_{\text{actual}} / [\text{fuel/air}]_{\text{stoichiometric}}$

Measured temperature profiles for these runs are given in Figure 3. The PFR temperatures either decrease or increase along its length depending on the degree of additional combustion occurring. At higher primary stage ϕ values, the heat produced in the second stage more than overcomes sensible losses. The experimental operability advantage of these losses is now clear.

Figure 4 presents measured and model-predicted NO levels for these runs in the PSR. The highest levels occur for the fuel-lean feeds. As the primary stage ϕ increases, the NO concentration drops dramatically. However, as expected, the CO level increases with a drop in CO₂, as shown in Figures 5 and 6 respectively. The injection of the secondary air, though, enhances CO conversion. Figure 7 dramatically illustrates that a minimum in NO at the PFR outlet exists for a PSR feed ϕ of 1.35. Though the 700 ppm level is twice the 350 ppm PSR concentration, it is still much lower than the PFR outlet NO level of 1800 ppm for the all fuel-lean base case ($\phi = 0.86$).

Preliminary results have been obtained on the simultaneous staged combustion of C₂H₄/CH₃Cl/CH₃NH₂. The feed CH₃NH₂/C₂H₄ ratio, primary stage ϕ , and overall ϕ were kept constant, while the feed CH₃Cl/C₂H₄ ratio was varied. Increasing the CH₃Cl loading results in a drop in NO concentration (Figure 8), which cannot be explained by the negligible drop in reactor temperature profiles as the chlorine content increases. Rate-of-production analysis will be used to identify the responsible chemical pathways.

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REFERENCES

- Beer, J. M. and Chigier, N. A., Combustion Aerodynamics, Krieger Publishing, Malabar, FL (1983).
- Beer, J. M., Jacques, M. T., Farmayan, W., and Taylor, B. R., *18th Symposium (Int.) on Combustion*, The Combustion Institute, Pittsburgh, PA, p. 101 (1981).
- Kee, R. J. and Miller, J., Sandia National Laboratories Report, SAND86-8841, Livermore, CA (1986).
- Miller, J. and Bowman, C., *Progress in Energy and Combustion Science*, vol. 15, p. 287 (1989).
- Nenniger, J. E., Chomiak, J., Kridiotis, A., Longwell, J. P., and Sarofim, A. F., *20th Symposium (Int.) on Combustion*, The Combustion Institute, Pittsburgh, PA (1984).
- Sun, W. H., Longwell, J. P., and Sarofim, A. F., 193th National Meeting of the American Chemical Society (1987).

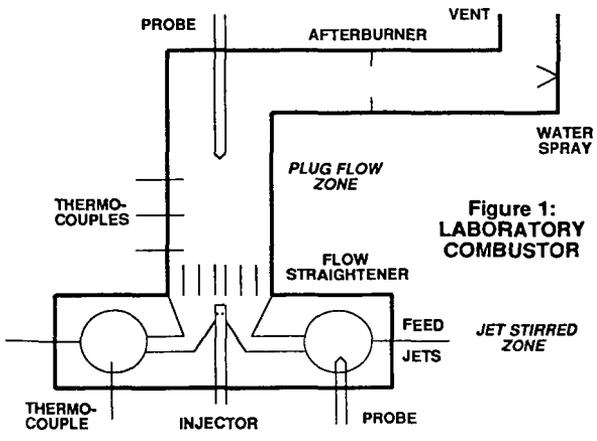


Figure 1: LABORATORY COMBUSTOR

Figure 2: STAGED COMBUSTION FACILITY

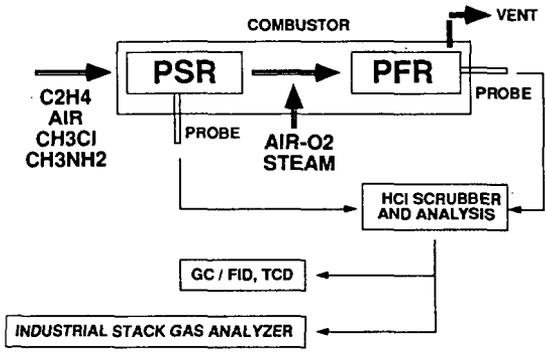


FIGURE 3

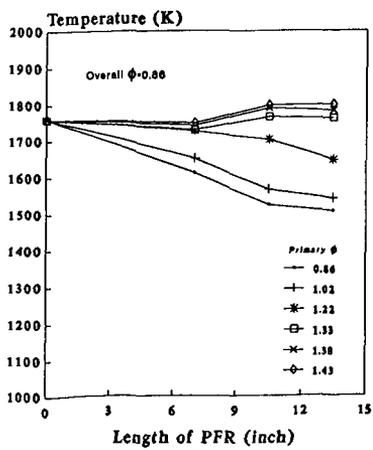


FIGURE 4

